First-Principles Study of Lead-Free A_3InX_6 (A = Rb, Cs; X = Cl, Br, I) Defect -Perovskites: Structural, Electronic, Optical, and Mechanical Properties

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$$n\lambda = 2dsin\theta \quad \text{(S1)}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{(S2)}$$

$$\alpha(\omega) = \sqrt{2\omega\left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right]^{\frac{1}{2}}} \quad \text{(S3)}$$

$$\sigma_1(\omega) = \frac{2\pi e^2\hbar}{m^2\omega\Omega}\sum_{k,v,c}\left|\langle\psi_{ck}|p|\psi_{vk}\rangle\right|^2\delta\left(E_{ck} - E_{vk} - \hbar\omega\right) \quad \text{(S4)}$$

$$\mathcal{E}(\omega) = \mathcal{E}_1(\omega) + jE_2(\omega) \quad \text{(S5)}$$

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}P\int_0^{\infty}\frac{\omega'\varepsilon_2(\omega')}{\omega'^2 - \omega^2}d\omega' \quad \text{(S6)}$$

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\langle\Psi_k^c|\hat{u}.\vec{r}|\Psi_k^v\rangle\right|^2\delta\left(E_k^c - E_k^v - E\right) \quad \text{(S7)}$$

$$R(\omega) = \frac{(\eta - 1)^2 + k^2}{(\eta + 1)^2 + k^2} \quad \text{(S8)}$$

$$\eta'(\omega) = \eta(\omega + i\,k(\omega) \quad \text{(S9)}$$

$$n(\omega) = \frac{1}{\sqrt{2}}\left[\left(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2\right)^{\frac{1}{2}} + \varepsilon_1(\omega)\right]^{\frac{1}{2}} \quad \text{(S10)}$$

$$k(\omega) = \frac{1}{\sqrt{2}}\left[\left(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2\right)^{\frac{1}{2}} - \varepsilon_1(\omega)\right]^{\frac{1}{2}} \quad \text{(S11)}$$

Table S1. Optimized structural parameters and atomic fractional coordinates of Rb_3InX_6 obtained from first-principles calculations.

Atom	**Wyckoff**	**x**	**y**	**z**
In	4a	0.0000	0.0000	0.0000
Rb	4b	0.5000	0.0000	0.0000
Rb	8c	0.2500	0.2500	0.7500

X (X= Cl, Br, I)	24e	0.219174	0.0000	0.0000

Table S2. Optimized structural parameters and atomic fractional coordinates of **Cs_3InX_6** obtained from first-principles calculations.

Atom	**Wyckoff**	**x**	**y**	**z**
In	4a	0.0000	0.0000	0.0000
Cs	4b	0.5000	0.0000	0.0000
Cs	8c	0.2500	0.2500	0.7500
X (X= Cl, Br, I)	24e	0.219174	0.0000	0.0000

Table S3. The energy band gap, lattice constants, unit cell volume & formation enthalpy of A_3InX_6 (A=Rb, Cs, and X=Cl, Br, I) Perovskites

Ref.	**Compounds**	**Band Gaps (E_g)**	**Lattice Constant, a(Å)**	**Functionals**
This work	Rb_3InCl_6	3.695	-	GGA-PBESOL
	Rb_3InBr_6	2.595	-	
	Rb_3InI_6	1.429	-	
	Cs_3InCl_6	3.801	-	
	Cs_3InBr_6	2.755	-	
	Cs_3InI_6	1.590	-	
	Rb_3InCl_6	5.004	-	Hybrid (HSE06)
	Rb_3InBr_6	3.892	-	
	Rb_3InI_6	2.550	-	
	Cs_3InCl_6	5.116	-	
	Cs_3InBr_6	4.038	-	
	Cs_3InI_6	2.556	-	
[1]	Na_3GaBr_6	1.991	7.747	GGA-PBE
	K_3GaBr_6	1.445	8.085	
	Na_3GaBr_6	2.602	-	mGGA-RSCAN
	K_3GaBr_6	1.985	-	
	Na_3GaBr_6	3.096	-	Hybrid (HSE06)
	K_3GaBr_6	2.567	-	
[2]	Cs_3InCl_6	1.45	-	

	Cs_3InBr_6	1.55	-	
	Cs_3InI_6	1.60	-	
	Cs_3TlCl_6	0.93	-	
	Cs_3TlBr_6	1.01	-	
	Cs_3InI_6	0.99	-	
[3]	Rb_3InCl_6	5.22	-	Experimental

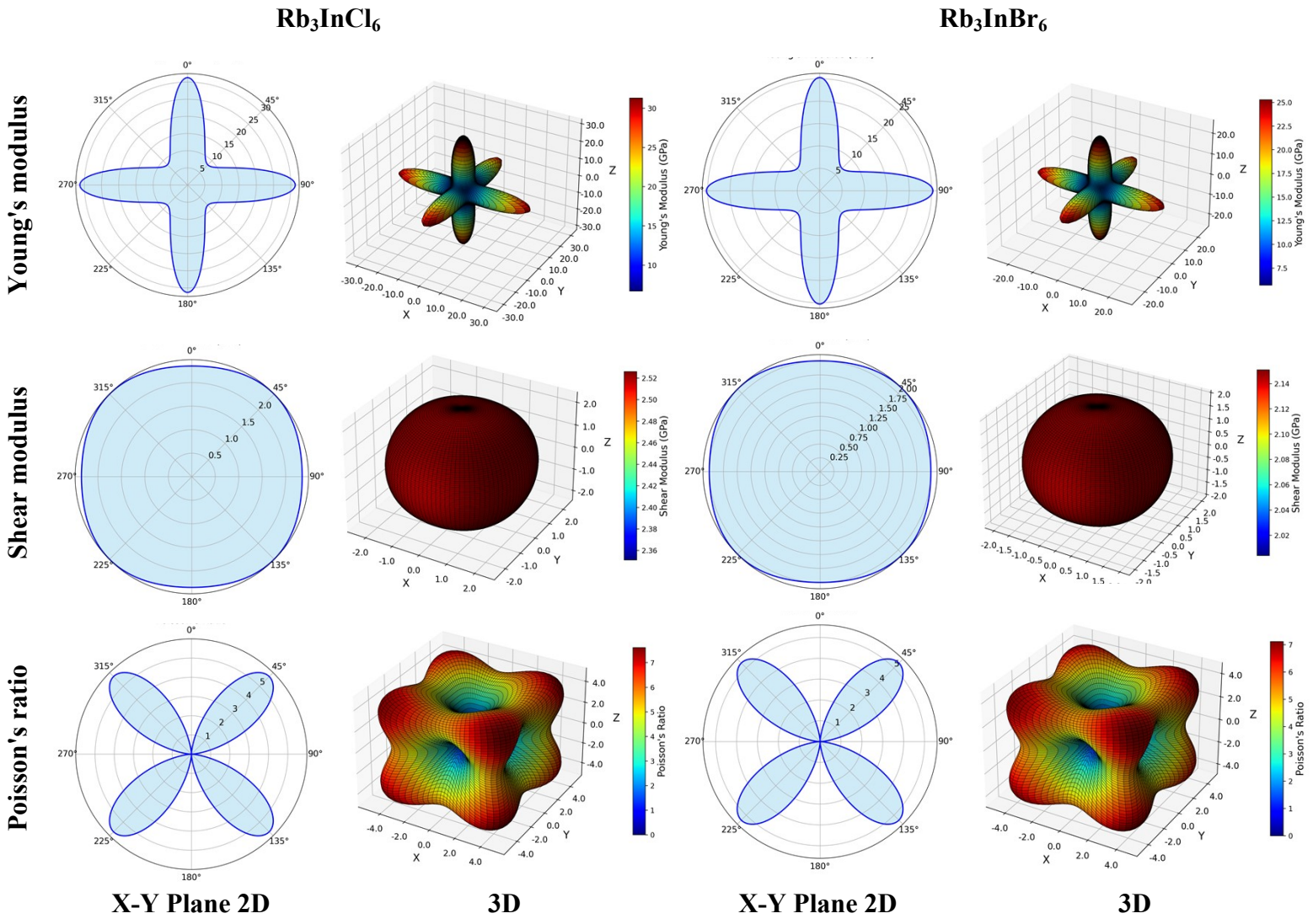

Figure S1. Graphical assessment of Rb_3InCl_6 and Rb_3InBr_6 Perovskites anisotropy showing 2D and 3D figures.

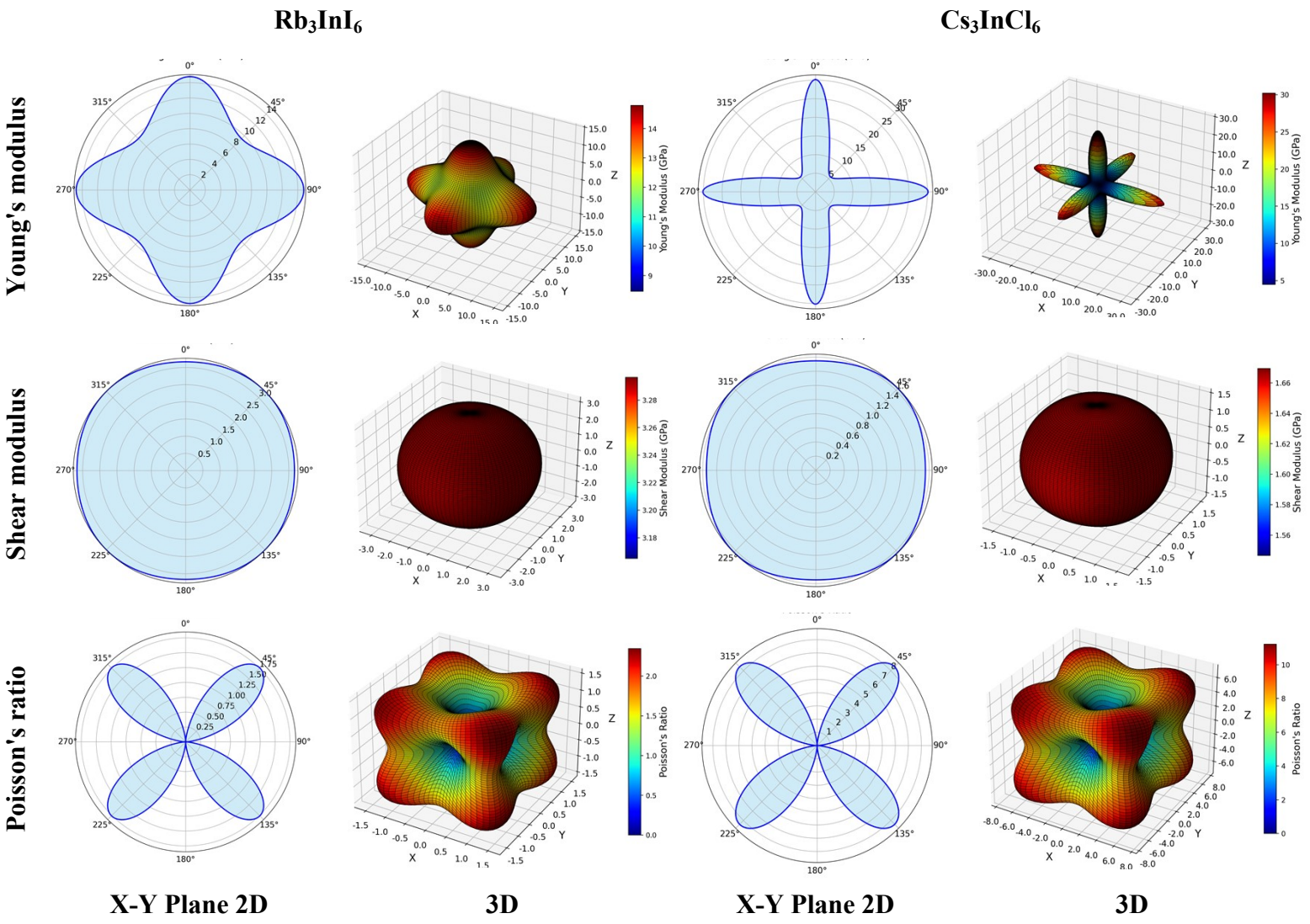

Figure S2. Graphical assessment of Rb_3InI_6 and Cs_3InCl_6 Perovskites anisotropy showing 2D and 3D figures.

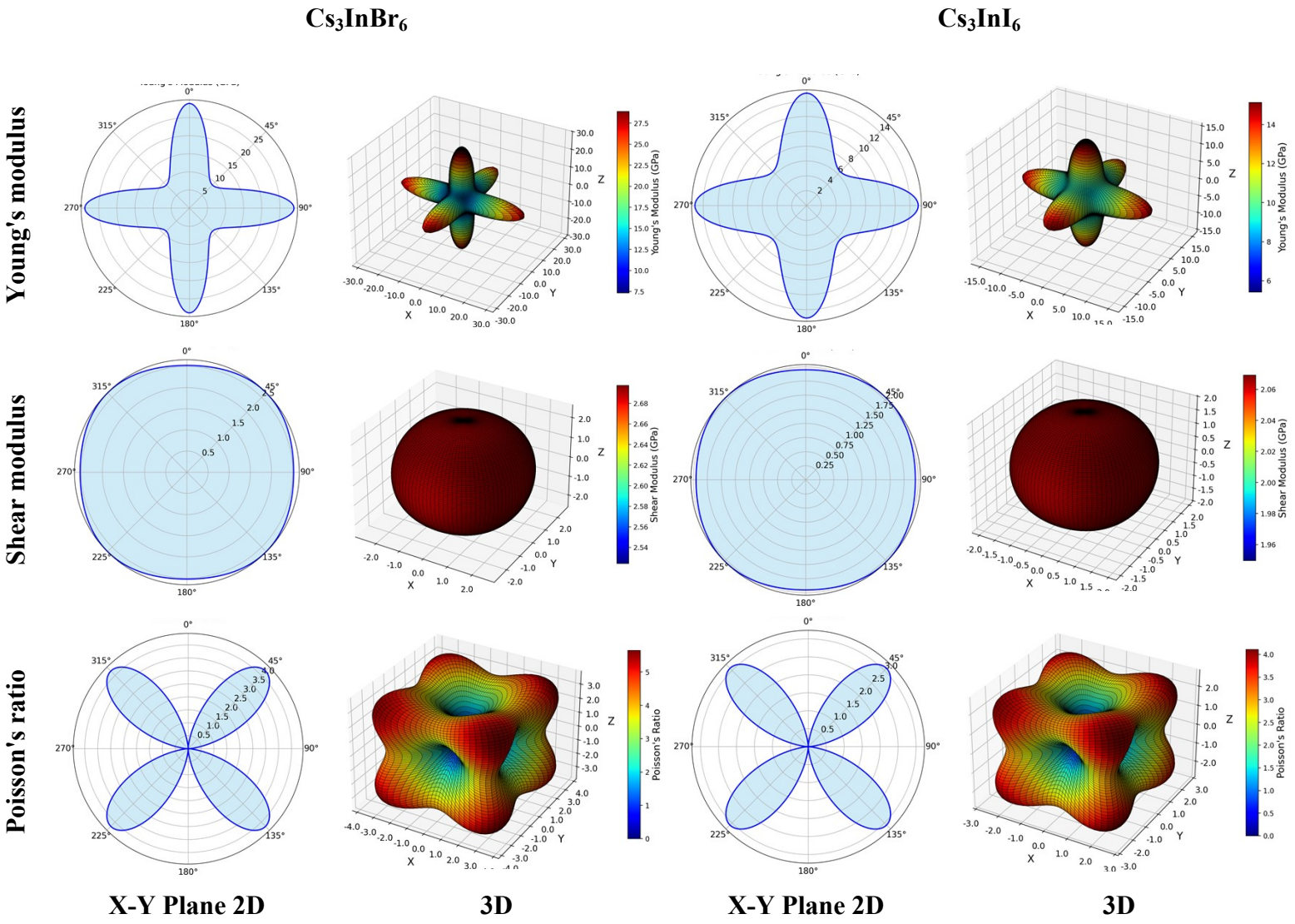

Figure S3. Graphical assessment of Cs_3InBr_6 and Cs_3InI_6 Perovskites anisotropy showing 2D and 3D figures.

Table S4. Mulliken and Hirshfeld charge analysis of different atoms of A_3InX_6 (A=Rb, Cs, and X=Cl, Br, I) Perovskites

Compound	Change	Species	Mulliken atomic populations	Mulliken	Hirshfeld

	spilling		s	P	d	f	Total	change	change
Rb_3InCl_6	0.11%	Rb (1)	2.11	6.18	0.45	0.00	8.73	0.27	0.17
		Rb (2)	1.99	5.98	0.11	0.00	8.08	0.92	0.33
		Rb (3)	1.99	5.98	0.11	0.00	8.08	0.92	0.33
		In	1.11	1.16	10.00	0.00	12.26	0.74	0.41
		Cl	1.94	5.53	0.00	0.00	7.47	-0.47	-0.23
Rb_3InBr_6	0.09%	Rb (1)	2.13	6.39	0.53	0.00	9.05	-0.05	0.16
		Rb (2)	2.03	6.15	0.20	0.00	8.38	0.62	0.32
		Rb (3)	2.03	6.15	0.20	0.00	8.38	0.62	0.32
		In	1.41	1.39	10.00	0.00	12.81	0.19	0.35
		Br	1.76	5.47	0.00	0.00	7.23	-0.23	-0.21
Rb_3InI_6	0.11%	Rb (1)	2.21	6.36	0.56	0.00	9.13	-0.13	0.14
		Rb (2)	2.08	6.14	0.18	0.00	8.40	0.60	0.32
		Rb (3)	2.08	6.14	0.18	0.00	8.40	0.60	0.32
		In	1.12	1.53	10.00	0.00	12.65	0.35	0.27
		I	1.83	5.41	0.00	0.00	7.24	-0.24	-0.20
Cs_3InCl_6	0.12%	Cs (1)	2.11	6.18	0.40	0.00	8.69	0.31	0.24
		Cs (2)	2.00	5.93	0.14	0.00	8.07	0.93	0.38
		Cs (3)	2.00	5.93	0.14	0.00	8.07	0.93	0.38
		In	1.13	1.14	10.00	0.00	12.26	0.74	0.42
		Cl	1.95	5.54	0.00	0.00	7.49	-0.49	-0.24
Cs_3InBr_6	0.10%	Cs (1)	2.14	6.39	0.47	0.00	9.00	-0.00	0.21
		Cs (2)	2.05	6.13	0.19	0.00	8.37	0.63	0.35
		Cs (3)	2.05	6.13	0.19	0.00	8.37	0.63	0.35
		In	1.36	1.38	10.00	0.00	12.74	0.26	0.35
		Br	1.78	5.48	0.00	0.00	7.25	-0.25	-0.21
Cs_3InI_6	0.10%	Cs (1)	2.19	6.33	0.51	0.00	9.03	-0.03	0.18
		Cs (2)	2.09	6.15	0.18	0.00	8.42	0.58	0.35
		Cs (3)	2.09	6.15	0.18	0.00	8.42	0.58	0.35
		In	1.14	1.51	10.00	0.00	12.65	0.35	0.28
		I	1.83	5.41	0.00	0.00	7.25	-0.25	-0.19

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